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EXAMINER
MULLIS, J.

ART UNIT	PAPER NUMBER
1207	7

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DATE MAILED: 03/14/96

This is a communication from the examiner in charge of your application.
COMMISSIONER OF PATENTS AND TRADEMARKS

- ☐ This application has been examined ☒ Responsive to communication filed on 10-3-95 ☐ This action is made final.
- A shortened statutory period for response to this action is set to expire 3 month(s), _____ days from the date of this letter.
Failure to respond within the period for response will cause the application to become abandoned. 35 U.S.C. 133

Part I THE FOLLOWING ATTACHMENT(S) ARE PART OF THIS ACTION:

- ☒ Notice of References Cited by Examiner, PTO-892.
- ☐ Notice of Art Cited by Applicant, PTO-1449.
- ☐ Information on How to Effect Drawing Changes, PTO-1474.

- ☐ Notice of Draftsman's Patent Drawing Review, PTO-948.
- ☐ Notice of Informal Patent Application, PTO-152.

Part II SUMMARY OF ACTION

- ☒ Claims 41-77 are pending in the application.
Of the above, claims _____ are withdrawn from consideration.
- ☒ Claims 1-40 have been cancelled.
- ☐ Claims _____ are allowed.
- ☒ Claims 40-87, 89-75 are rejected.
- ☒ Claims 48 are objected to.
- ☐ Claims _____ are subject to restriction or election requirement.
- ☐ This application has been filed with Informal drawings under 37 C.F.R. 1.85 which are acceptable for examination purposes.
- ☐ Formal drawings are required in response to this Office action.
- ☐ The corrected or substitute drawings have been received on _____. Under 37 C.F.R. 1.84 these drawings are ☐ acceptable; ☐ not acceptable (see explanation or Notice of Draftsman's Patent Drawing Review, PTO-948).
- ☐ The proposed additional or substitute sheet(s) of drawings, filed on _____, has (have) been ☐ approved by the examiner; ☐ disapproved by the examiner (see explanation).
- ☐ The proposed drawing correction, filed _____, has been ☐ approved; ☐ disapproved (see explanation).
- ☐ Acknowledgement is made of the claim for priority under 35 U.S.C. 119. The certified copy has ☐ been received ☐ not been received ☐ been filed in parent application, serial no. _____, filed on _____.
- ☐ Since this application appears to be in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under Ex parte Quayle, 1935 C.D. 11; 453 O.G. 213.
- ☐ Other

EXAMINER'S ACTION

Serial Number: 08/367,370

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Art Unit: 1207

Any rejections/objections not appearing in this Office action have been withdrawn.

The following is a quotation of 35 U.S.C. § 103 which forms the basis for all obviousness rejections set forth in this Office action:

A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

Subject matter developed by another person, which qualifies as prior art only under subsection (f) or (g) of section 102 of this title, shall not preclude patentability under this section where the subject matter and the claimed invention were, at the time the invention was made, owned by the same person or subject to an obligation of assignment to the same person.

Claims 40-47 and 49-75 are rejected under 35 U.S.C. § 103 as being unpatentable over Whistler et al., Ind. Eng. Chem. 38, 796 (1944) in view of Lotti (Polymer Bulletin Article, cited by applicants) and Wolff et al. (Ind. and Eng. Article "Mixed Esters of Amylose, cited by applicants, Lipinsky (WO 92/20738), Elion (USP 5,205,863) Lay et al. (USP 5,095,054) Buchanan

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-3-

Art Unit: 1207

(WO 92/09654) and (Klug USP 3,117,014), Fordyce et al. (Ind. Eng. Chem., p. 1053-1060, 1960)

See the previous Office action at page 4, lines 5 et seq.

Applicant's arguments filed 10-3-95 have been fully considered but they are not deemed to be persuasive. Applicants' remarks regarding each of the references are piecemeal analysis.

None of the claims as amended are supported by 07/957,924 so the effective filing date for all of the instant claims are 12-22-92.

A copy of Fordyce is being provided with this Office action.

The motivation to combine the teachings of the secondary references with Whistler is to extend the benefits of the secondary references to the primary reference. Whistler had no problem making films as long as they were plasticized.

Serial Number: 08/367,370

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Art Unit: 1207

Claim 48 is objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims.

Bloembergen et al. (USP 5,462,983), cited of interest discloses applicants' composition. Note patent claim 1.


This action is not being made FINAL.

A facsimile center has been established in Group 1200, room 3C10. The hours of operation are Monday through Friday, 8:45 AM to 4:45 PM. The telecopier numbers for accessing the facsimile machine are (703) 308-4556 or 305-3592.

Any inquiry concerning this communication should be directed to Examiner Jeffrey Mullis at telephone number (703) 308-2820.

**JEFFREY C. MULLIS
PRIMARY EXAMINER
GROUP 1200**

**MULLIS; aco
February 28, 1996
March 5, 1996**



What's Behind



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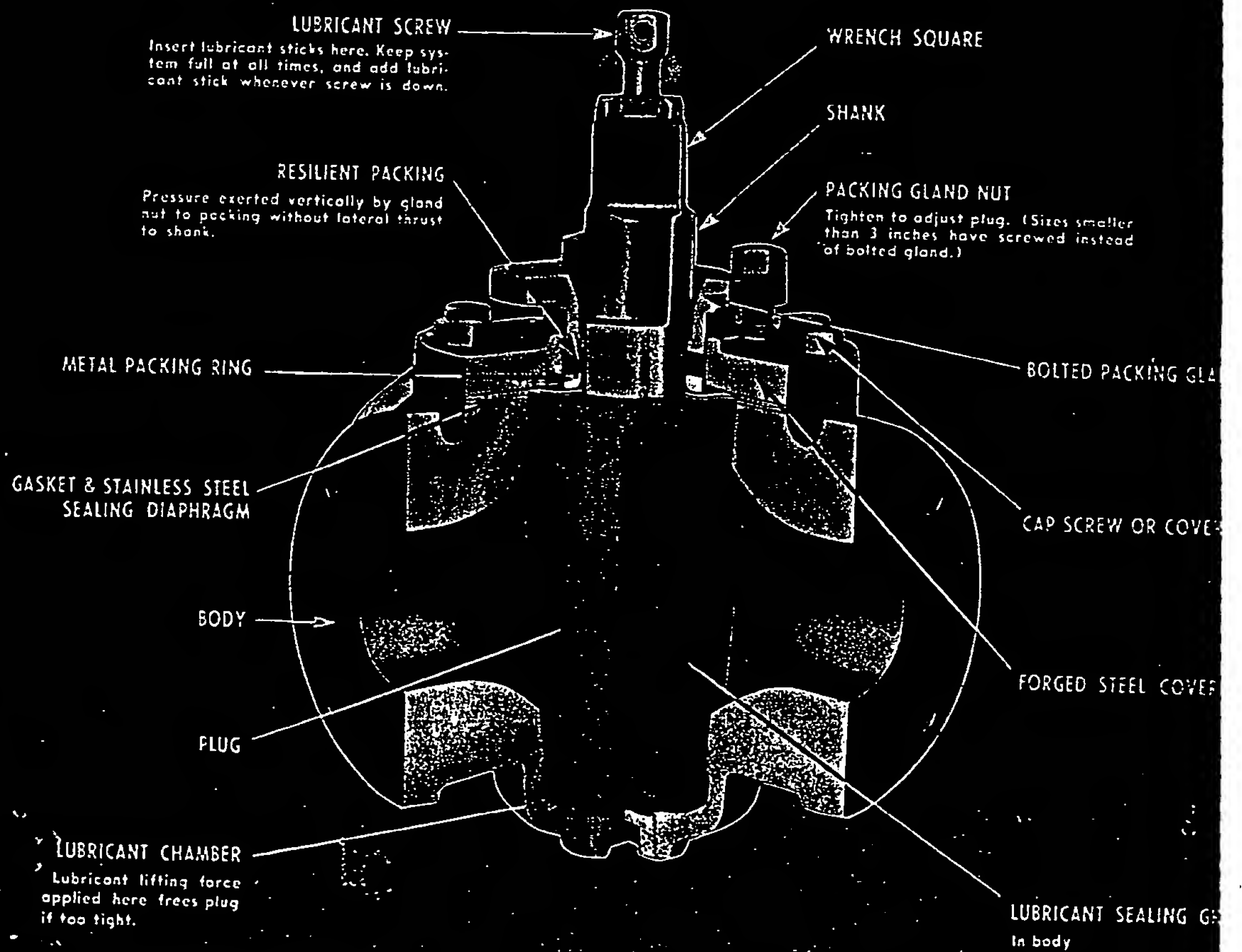
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NORDSTROM



Plasticizers for Cellulose Acetate and Cellulose Acetate Butyrate

Most commercial uses of cellulose acetate require the incorporation of some quantity of plasticizer for satisfactory behavior of the product. The physical characteristics of forty plasticizers have been investigated to supply suitable data for evaluation of plasticized compositions for different uses. Plasticizer retention curves indicate that most compounds which are readily compatible with cellulose acetate are rapidly removed from the composition unless used in relatively small quantities. Estimated values of maximum permanent compatibility have been determined from accelerated retention curves.

Cellulose mixed esters of acetic and butyric acids offer increased compatibility with plasticizers of outstanding water resistance and retention characteristics. Products of 35-40 per cent butyryl content are especially suited for molding compositions, giving adequate flow characteristics with low plasticizer concentrations. Plastics of this type offer improved weathering qualities over those of similar flow temperatures made from cellulose acetate.

WHEN cellulose acetate or its related compounds, such as cellulose acetate butyrate, are used in the manufacture of an article, whether the operation be molding, coating of fabrics, films, lacquers, or electrical insulation, in order for the product to be acceptable, some quantity of a suitable plasticizer must be incorporated with it. In the field of molding its presence is necessary to permit sufficient flow under the influence of heat and pressure; coated fabrics require the plasticizer for flexibility; films and lacquer coatings, for most purposes, find improved water resistance and freedom from brittleness by virtue of plasticizers; and for electrical insulation greater latitude of workability in extrusion of coatings or winding of tape is obtained by use of a well plasticized composition.

Numerous compounds have been suggested as plasticizers for cellulose acetate. From even a brief review of the literature, a list of over two hundred proposed materials may be compiled. It remains for the user to determine which among them would be most serviceable for a given case.

C. R. FORDYCE

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Even among widely diversified uses of cellulose ester plastics, there are several common requirements of the plasticizer to be present. It must be compatible with the cellulose derivative in appreciable quantity, must be retained throughout a reasonable period of aging, must remain colorless, and must not induce acidity in the composition. From the large number of plasticizers which have been proposed, it is possible to discard a great many compounds immediately as definitely unsatisfactory in one or more of the above mentioned requirements. More critical examination shows that comparatively few compounds are definitely valuable plasticizers. In this way we may select from the list those plasticizers which appear important enough from the commercial standpoint to warrant more critical study. A list of plasticizers so chosen has been investigated in detail in an effort to collect data which would enable one to choose the most suitable type of compound for any given application.

The standard physical characteristics of plasticizers, including melting and boiling points, specific gravity, refractive index, etc., are of definite value in predicting their commercial importance. In addition to these data, there are a number of other important characteristics of the compounds which are more directly related to their commercial application.

In the discussion and tables of plasticizers, no mention will be made of the patent situation regarding individual compounds or mixtures. The statements will serve only as suggestions and should not be considered as recommendations of the use of any compounds in violation of patents now in force or which may issue in the future. It is recommended that the patent situation be reviewed carefully before any of these compounds is placed in actual use.

Physical Properties and Acidity

Most cellulose acetate plasticizers are insoluble in water, and exact measurement of the slight degree to which they dissolve may therefore appear to be of minor importance. It has been found, however, that several useful characteristics of plasticizers parallel this property, and compounds of very low water solubility should be insisted upon if the best possible plasticizer is desirable. The water solubility of each plasticizer of the group chosen for this study has been determined in order that all values may be comparable. Results

TABLE I. PROPERTIES OF CELLULOSE ACETATE PLASTICIZERS

	Mol. Weight	M. P., ° C.	B. P., ° C.	Sp. Gr.	Refractive Index	% Water Soly.	Free Acidity ^a	Boiling Water Stability
Benzophenone	182	48	305	1.111	1.602	0.006	0.05	0.15
Butyl phthalyl butyl glycollate	336	< -45	219(5 mm.)	1.097	1.488	0.018	0.70	34.50
Camphor	152	178	204	0.990	...	0.170	0.60	...
<i>o</i> -Cresyl- <i>p</i> -toluene sulfonate	262	52.5	...	1.207	1.558	0.003	0.04	0.06
Cyclohexyl- <i>p</i> -toluene sulfonamide	253	86	1.542	0.006	0.46	0.04
Diamyl phthalate	306	< -55	342	1.022	1.488	0.010	0.27	0.93
Dibutyl phthalate	278	-35	325	1.050	1.490	0.013	0.14	0.16
Dibutyl sebacate	314	...	345	0.933	1.493	0.005	1.05	0.05
Dibutyl succinate	230	-19	255	0.974	1.428	0.023	0.90	27.40
Dibutyl tartrate	262	22	312	1.098	1.445	0.485	2.75	216.25
Diethoxyethyl adipate	290	< -70	...	1.036	1.439	0.248	3.64	44.56
Diethoxyethyl phthalate	310	34	345	1.123	1.492	0.195	2.15	3.05
Diethyl adipate	202	-14	245	1.002	1.426	0.060	4.45	14.5
Diethylene glycol dipropionate	218	< -82	165(4 mm.)	1.056	1.429	3.60	0.52	591.5
Diethyl phthalate	222	-0.3	295	1.118	1.499	0.150	0.07	0.13
Diethyl sebacate	258	1.3	308	0.965	1.435	0.018	0.52	0.08
Diethyl succinate	174	-22	218	1.048	1.419	0.190	0.09	308.0
Diethyl tartrate	206	17	280	1.199	1.445	> 50	1.01	912.0
Dimethoxyethyl adipate	262	-16	...	1.075	1.439	1.420	34.2	613.9
Dimethoxyethyl phthalate	282	< -60	209-61(20 mm.)	1.17	1.500	0.838	1.40	4.40
Dimethyl phthalate	194	0	285	1.193	1.513	0.305	0.20	1.00
Dipropyl phthalate	250	-31	158(4 mm.)	1.071	1.494	0.015	0.65	0.15
Ethyl benzoyl benzoate	254	58	355	1.155	1.573	0.010	0.30	1.12
Ethylene glycol diacetate	146	< -78	186	1.128	1.414	1.815	0.14	1229.0
Ethylene glycol dibutyrate	202	< -80	240	1.024	1.424	0.050	9.16	1.55
Ethylene glycol dipropionate	174	< -80	211	1.054	1.419	0.160	0.88	49.31
Ethyl phthalyl ethyl glycollate	280	< -35	190(5 mm.)	1.177	1.498	0.050	0.50	378.0
Methyl benzoyl benzoate	240	52	351	1.190	1.587	0.005	3.20	1.30
Methyl phthalyl ethyl glycollate	266	< -35	189(5 mm.)	1.220	1.503	0.053	2.30	106.20
<i>o</i> - & <i>p</i> -Toluene ethyl sulfonamide	199	18	...	1.190	1.540	0.140	4.30	0.40
Triacetin	218	< -40	259	1.161	1.429	0.685	1.84	1015.0
Tributyl citrate	360	< -55	...	1.040	1.444	0.008	12.30	9.80
Tributyl phosphate	266	< -20	289	0.976	1.421	0.033	3.60	3.50
Tributyrin	302	< -70	287	1.032	1.434	0.010	0.44	13.06
Tricresyl phosphate	368	< -35	295(13 mm.)	1.175	1.556	0.008	0.55	0.05
Triethylene glycol diacetate	234	< -60	300	1.111	1.437	> 50	2.12	676.0
Triethylene glycol dibutyrate	290	< -70	154-60(2 mm.)	1.033	1.437	0.800	0.60	3.90
Triethylene glycol dipropionate	262	< -60	138-42(2 mm.)	1.066	1.436	6.70	3.10	533.0
Triphenyl phosphate	326	48.5	245(11 mm.)	1.185	1.563	0.002	0.21	0.09
Tripropionin	260	< -50	177-82(20 mm.)	1.078	1.431	0.313	0.42	52.58

^a These values represent the quality of the various plasticizers as available for commercial use, and upon which the boiling water stability tests were run.

of these tests are recorded, together with other physical properties of the compounds in Table I.

An important factor in the evaluation of plasticizers is the acidity which may be present in the material or which may be developed during use. The amount of free acidity may be conveniently determined by direct titration. The degree of stability toward development of further acidity during use must be determined by tests designed for that purpose. A satisfactory test is one which measures the acidity developed under moist conditions and involves treatment of the plasticizer with boiling water for a number of hours. The results may be recorded in terms of quantity of standard alkali required to neutralize the acidity developed during boiling and may be designated the "boiling water stability" of the plasticizer. Compounds giving high values in this test should be avoided, especially in uses which encounter contact with water or exposure to moist conditions. It has not been possible to obtain a direct correlation between these values and the aging qualities of plasticized compositions, except that, in general, plasticizers which show both high acidity values with boiling water and appreciable water solubility are easily removed from plasticized compositions during aging and tend to produce brittleness. If the water solubility is very low, the boiling water stability appears to be less important. In Table I are recorded results of this test, together with free acidity values of the materials.

Maximum Compatibility

More direct measurement of the durability of plasticized cellulose ester compositions may be made by examination of films containing varying quantities of the plasticizers to be tested. These may be prepared most easily by evaporation of solutions of the cellulose ester and plasticizer mixtures to produce films of desired thickness. If suitable precautions

are taken to make sure of the actual plasticizer contents of the test samples, comparable results are obtained on solvent-coated and molded compositions. When films or coatings are obtained by evaporation of solutions in organic solvents, the unexpectedly high volatility of some compounds results in a considerable loss of plasticizer even by the time the volatile solvent is driven off. For this reason, while large amounts of such plasticizers may be added to the solutions as prepared, the actual maximum concentration which can be realized in the dried film may be comparatively small. As a measure of the usable range of composition of these materials, the maximum quantities of plasticizers which may be incorporated with high (40.5 per cent), medium (38.5 per cent), and low (37.5 per cent) acetyl cellulose acetate to give clear, homogenous films have been determined; care has been taken to correct for unexpected volatility by determining the plasticizer content by analysis.

The maximum amount of a given plasticizer which may be successfully employed with cellulose acetate depends to some extent upon the behavior expected from the resulting composition. If the only requirement is that a uniform, homogenous composition be obtained, then comparatively high percentages of a number of materials may be used. On the other hand, if it is important that the composition withstand a reasonable amount of aging without appreciable loss of plasticizer, greater precaution is necessary.

The values of maximum compatibility give no indication of retention during aging. In practically all cases use of maximum quantities of plasticizer in a composition would result in rapid loss of plasticizer from the finished product during use. This is demonstrated in the curves of Figure 1, which show the loss of diethyl phthalate from films containing increasing quantities of the plasticizer, when exposed to weather conditions on the roof. After long periods the plas-

TABLE II. RETENTION OF PLASTICIZERS BY CELLULOSE ACETATE (ACETYL 40.5 PER CENT)

	0	Roof, Aug.-Nov., 1938					Oven, 100° C.				Water Bath, 40° C.			
		20 hr.	60 hr.	1 wk.	1 mo.	3 mo.	20 hr.	60 hr.	100 hr.	160 hr.	20 hr.	60 hr.	100 hr.	160 hr.
Benzophenone	49	45	41	39	53	51	17	12	10	9	19	12	10	8
Butyl phthalyl butyl glycolate	55	55	55	54	53	51	17	12	10	9	19	12	10	8
Campbor	7	5	5	5	5	5	24	24	18	12	49	39	34	28
<i>o</i> -Cresyl- <i>p</i> -toluene sulfonate	35	34	34	32	25	21	24	21	19	14	30	27	26	24
Cyclohexyl- <i>p</i> -toluene sulfonamide	35	32	32	31	31	31	29	27	25	22	29	28	27	26
Diamyl phthalate	19	19	18	18	16	16	15	15	15	14	18	18	17	17
Dibutyl phthalate	32	32	31	30	28	11	20	19	18	17	29	27	26	25
Dibutyl succinate	23	15	9	7	5	3	3	3	3	3	4	1	1	0
Dibutyl tartrate	54	47	43	40	34	6	22	18	17	16	23	21	19	17
Diethoxyethyl adipate	35	22	14	10	9	6	17	9	7	6	5	4	4	3
Diethoxyethyl phthalate	56	48	43	40	38	38	38	9	7	6	25	19	16	14
Diethyl adipate	21	4	3	3	1	1	6	6	6	5	1	0	0	0
Diethylene glycol dipropionate	36	5	4	2	1	1	6	6	6	5	1	0	0	0
Diethyl phthalate	53	41	36	32	30	26	21	18	18	17	26	22	19	14
Diethyl sebacate	17	15	13	12	10	6	7	7	6	6	7	4	3	2
Diethyl succinate	9	3	2	1	0	0	4	3	3	2	0	0	0	0
Diethyl tartrate	49	10	10	9	7	4	16	14	14	12	5	5	4	4
Dimethoxyethyl adipate	53	23	14	10	9	6	18	12	11	8	5	5	5	5
Dimethoxyethyl phthalate	61	53	48	45	41	34	45	38	34	31	28	20	16	14
Dimethyl phthalate	42	29	27	25	24	20	16	14	13	12	17	11	8	6
Dipropyl phthalate	60	53	49	46	37	32	22	21	20	19	33	28	26	24
Ethyl benzoate	60	59	59	58	Brittle	...	40	31	28	26	50	46	44	39
Ethylene glycol diacetate	9	3	2	1	0	0	4	3	2	2	0	0	0	0
Ethylene glycol dibutyrate	15	4	3	3	2	2	5	4	4	4	1	0	0	0
Ethylene glycol dipropionate	10	3	2	2	1	1	4	3	3	3	0	0	0	0
Ethyl phthalyl ethyl glycolate	59	57	56	55	53	47	29	27	25	21	38	31	25	21
Methyl benzoate	61	57	57	56	Brittle	...	36	33	32	29	52	49	46	42
Methyl phthalyl ethyl glycolate	57	54	53	52	46	43	38	31	29	27	38	29	24	18
<i>o</i> - & <i>p</i> -Toluene ethyl sulfonamide	58	51	49	47	44	40	37	29	26	25	33	24	20	16
Triacetin	43	29	23	20	15	13	14	12	11	10	12	9	8	6
Tributyl citrate	62	58	56	54	50	43	32	25	24	22	34	28	27	24
Tributyl phosphate	40	28	27	23	18	15	14	13	12	12	15	14	12	9
Tributylin	58	49	47	44	37	28	19	18	18	17	25	22	20	17
Tricresyl phosphate	21	21	20	18	18	17	20	19	18	17	18	18	18	17
Triethylene glycol diacetate	51	10	9	8	6	4	14	12	11	10	5	5	5	4
Triethylene glycol dibutyrate	56	32	25	22	17	7	14	12	12	11	6	6	5	5
Triethylene glycol dipropionate	53	22	16	14	11	7	14	11	10	9	6	6	5	4
Triphenyl phosphate	31	29	29	28	28	28	26	23	22	21	27	26	24	23
Tripropionin	55	39	37	34	27	23	19	17	16	14	21	17	15	12

ticizer contents tend to fall to a common level, which is considerably below the maximum compatibility value.

Use of accelerated tests gives even more striking evidence of this behavior. The curves of Figure 2 illustrate the effect of immersion in water at 40° C. and incubation in an oven at 100° C. on the diethyl phthalate content of films. In each case there is a rapid initial loss of plasticizer, followed by a continued more gradual loss at an approximately common level. This suggests that there are two causes of loss of plasticizer; the first is a rapid loss due to excessive quantity, and the second a more gradual loss due possibly to vapor pressure of the compound or to rate of diffusion to the surface. The water immersion and oven incubation tests give similar curves and level off at comparatively equal values.

The behavior of diethyl phthalate is typical of practically all the plasticizers tested. The effect of water solubility is noticeable. Plasticizers of very low water solubility are retained better in the water bath than in oven incubation; those whose water solubility exceeds a value of approximately 0.03 per cent are retained to a somewhat lesser degree in the water bath.

The rapid loss of a considerable amount of plasticizer from cellulose acetate compositions explains undesirable behavior of the material in a number of uses in which high quantities of plasticizer are employed. Molded articles in such cases tend to warp or buckle

because of uneven loss of plasticizer; soft plastics such as those used in laminated glass tend to shrink and make edge sealing necessary; and surfaces in general are dull in appearance rather than brilliant because of continued diffusion of plasticizer to the surface.

Permanent Compatibility

To eliminate difficulties of this type and enable one to limit the plasticizer in quantity to that which will be retained with reasonable permanence, it becomes necessary to consider instead of maximum compatibility the "maximum permanent compatibility" of the plasticizers. A useful figure for these values may be obtained by projecting the lower portions of the water immersion curves, as given in Figure 2, back to the vertical axis. A figure is thus obtained representing the maximum amount of plasticizer which would leave the composition comparatively slowly upon aging, and which should be satisfactory for most purposes.

To obtain these values, films approximately 0.005 inch (0.127 mm.) thick were prepared containing

50-60 per cent plasticizer except in cases of limited compatibility, where lesser quantities were used. They were tested for plasticizer loss on the roof, in water at 40° C., and in the 100° C. oven. From the data obtained (Table II), curves were plotted and maximum permanent compatibilities

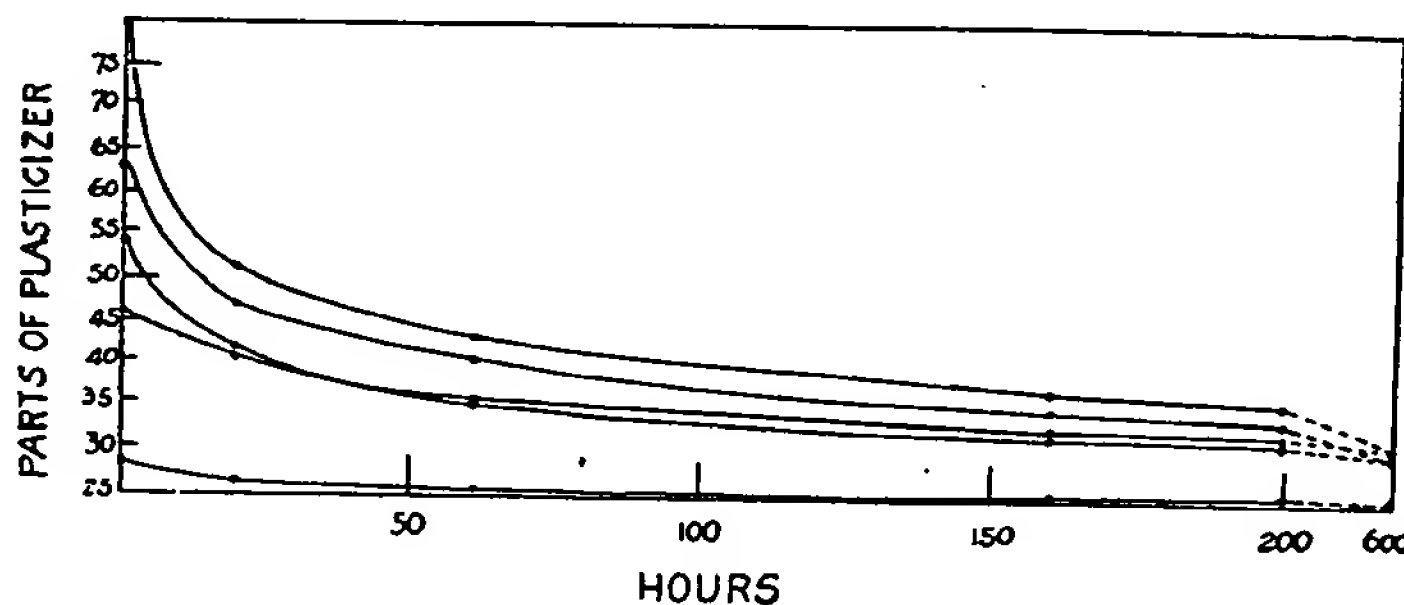


FIGURE 1. RETENTION OF DIETHYL PHTHALATE IN CELLULOSE ACETATE FILMS UNDER OUT-OF-DOOR EXPOSURE

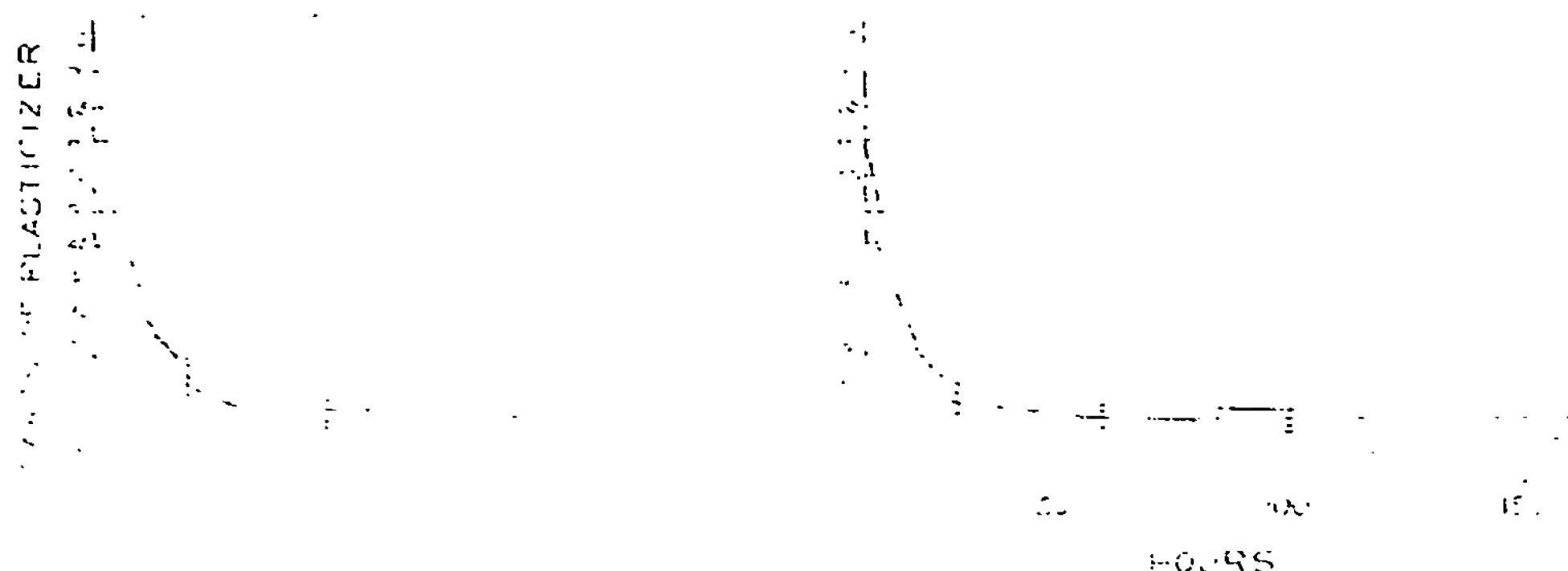


FIGURE 2. RETENTION OF DIETHYL PHTHALATE IN CELLULOSE ACETATE FILMS IMMERSSED IN WATER AT 100° C. (left) AND INCUBATED AT 100° C. (right)

estimated. Typical curves are given in Figure 3. Comparison of the curves for methyl, ethyl, propyl, butyl, and amyl phthalates shows the limitation in quantity which may be used in the lower members of the series because of rapid loss of plasticizer, while the butyl and amyl esters, although much better retained in the films, are confined because of limited compatibility to comparatively low concentrations. Methyl phthalyl ethyl and ethyl phthalyl ethyl glycolates are compatible with cellulose acetate in high proportions and are outstanding in aging properties on the roof, although in accelerated tests there is con-

tinued loss of material. This would indicate that they should be satisfactory in high proportions for conditions of exposure to the atmosphere, but would probably change in composition at elevated temperatures or if exposed to water. A great many materials are outstandingly inferior in plasticizer retention, since they are rapidly reduced to little or no plasticizer upon exposure to either roof or accelerated tests. The curves for triethylene glycol dipropionate and dimethoxyethyl adipate are illustrative of this behavior.

A summary of the behavior of the entire group of plasticizers may be obtained from Table III. The first three columns give the proportions of plasticizers used in preparing the cellulose acetate solutions to be coated into films. They represent the maximum amounts of plasticizer which would give clear films with no "sweating out", except in cases of extremely high compatibility for which equal quantities of cellulose acetate and plasticizer were used. The next three columns list the quantities of plasticizer in the films after evaporation of volatile solvent, as found by analysis. The last column gives maximum permanent compatibilities as determined from the data in Table II, by construction of curves and projection of the lower portions of the water immersion curves to the vertical axes.

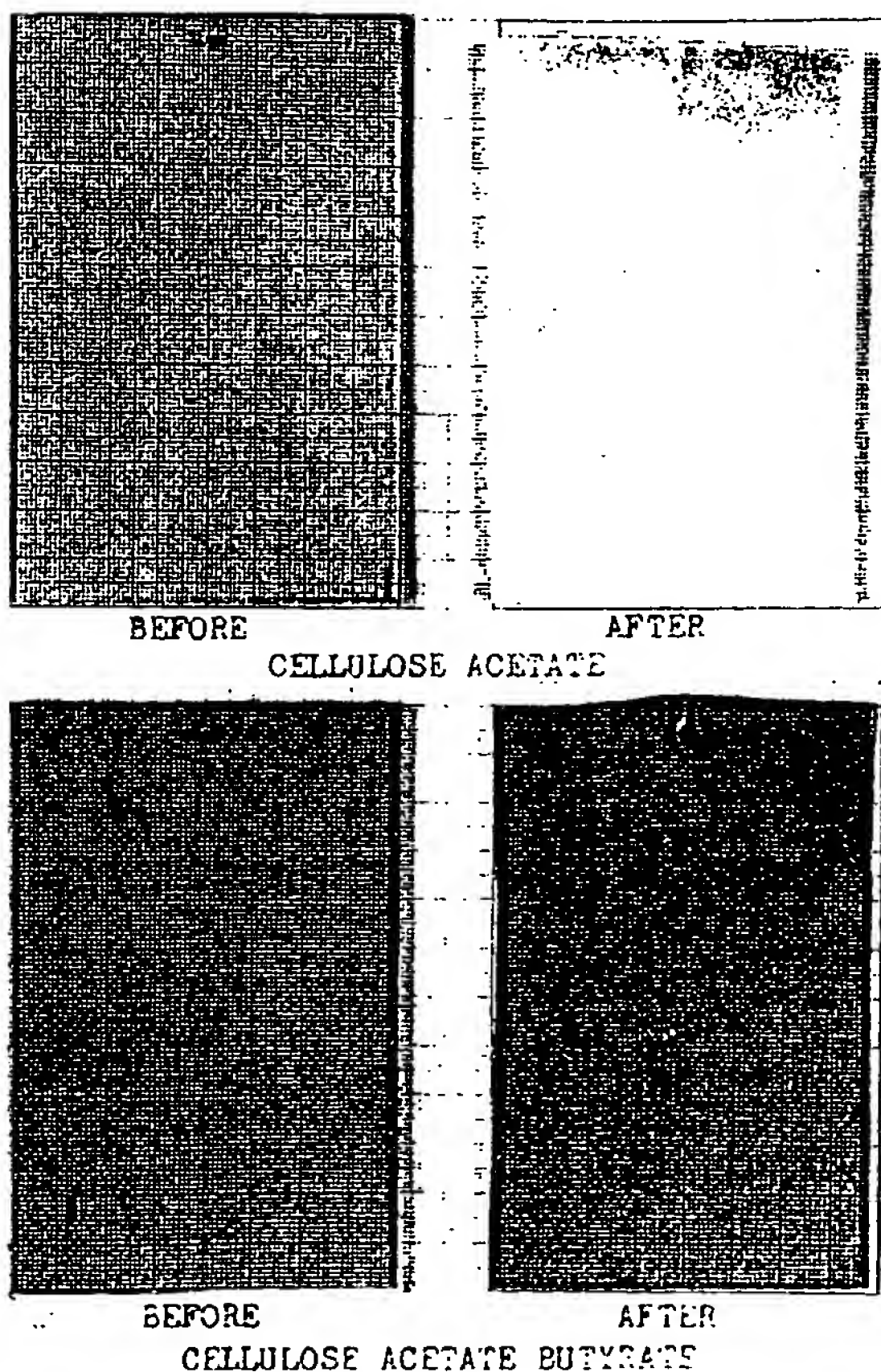
These results indicate that for most commercial applications it would be advisable to employ quantities of plasticizer well below the maximum permanent compatibility values and thus eliminate the disadvantages which arise from continual loss of plasticizer from the product.

For many uses, such as molding powders which require high concentrations of plasticizer for suitable flow during the molding operation, it becomes apparent that, with cellulose acetate, concentrations of plasticizer above that which will be permanently retained must be used to permit the required latitude of workability. As a result, this class of molding composition must acknowledge certain limitations of durability in regard to warping, surface luster, and other related qualities.

Attempts to improve the quality of these plastics must involve either search for a more suitable plasticizer which will exhibit hitherto unattained retention, or modification of the cellulose ester in such a way that existing plasticizers will be satisfactory.

Mixed Esters

Interesting possibilities in development of more suitable cellulose derivatives have been brought to light among cellulose mixed esters of acetic and butyric acids. These cellulose esters include a group of products which may vary in composition by modification of the proportions of combined acetic and butyric acids, as well as variation in degree of hydrolysis.



APPEARANCE OF CELLULOSE ACETATE (TENITE I) AND CELLULOSE ACETATE BUTYRATE (TENITE II) MOLDED PLASTICS, BEFORE AND AFTER IMMERSION FOR 6 HOURS IN BOILING WATER

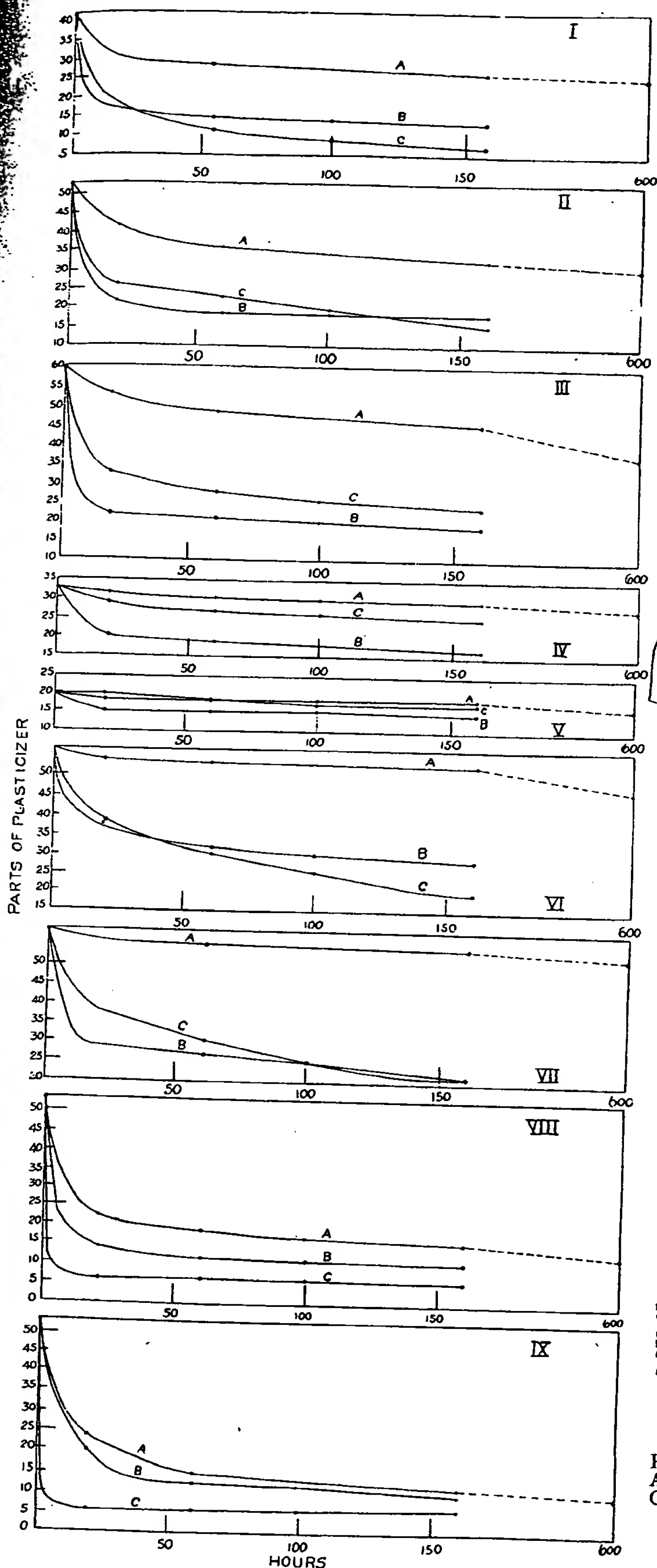


FIGURE 3. RETENTION OF PLASTICIZERS IN CELLULOSE ACETATE FILMS

A, Roof exposure; B, oven, 100° C.; C, water, 40° C.; I, dimethyl phthalate; II, diethyl phthalate; III, dipropyl phthalate; IV, dibutyl phthalate; V, diamyl phthalate; VI, methyl phthalyl ethyl glycollate; VII, ethyl phthalyl ethyl glycollate; VIII, triethylene glycol dipropionate; IX, dimethoxyethyl adipate

Cellulose acetate butyrate of 35-40 per cent butyryl content is particularly suitable for molding compositions in several ways. The product is more compatible with highly water-resistant and non-volatile plasticizers than cellulose acetate, and in this way presents a greater choice of molding composition. At the same time these plasticizers are retained much more permanently and in higher concentrations than those commonly used with cellulose acetate. Figure 4 gives plasticizer retention curves for cellulose acetate butyrate of 37 per cent butyryl and 13 per cent acetyl content, showing the larger quantities of plasticizer which will remain permanently in the composition than would be possible with cellulose acetate.

In addition to these qualities, the cellulose ester exhibits suitable flow characteristics with very small quantities of plasticizer, which permits workable compositions well below the maximum permanent concentration. In Table V are recorded molding characteristics and physical properties of this cellulose ester with a variety of plasticizers and, for comparison, similar data for cellulose acetate of 38.5 per cent acetyl content. From 22.6 to 37.8 per cent of dimethyl phthalate and 38.7 to 59.7 per cent of diethyl phthalate are required to produce flow temperature ranges of 307° to 266° F. (152.8° to 130° C.) with cellulose acetate; the acetate butyrate exhibits the same degree of flow with 6.3 to 15.8 per cent and 7.0 to 17.0 per cent, respectively. Dimethoxyethyl phthalate behaves similarly. These measurements were made on plastic compositions formed without use of volatile solvents. Flow temperature curves were plotted covering, in each case, a range of plasticizer content from which the tabulated data were obtained.

Table VI shows similar measurements on cellulose acetate butyrate, using plasticizers which are not sufficiently compatible with cellulose acetate to permit successful molding. Comparison of

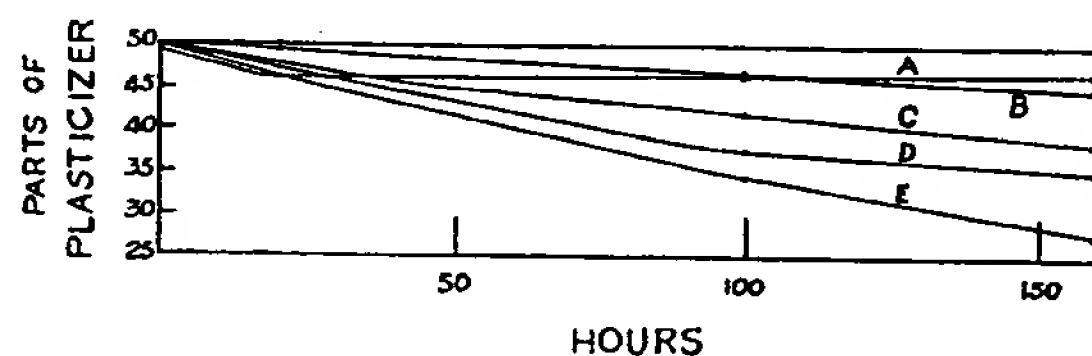


FIGURE 4. RETENTION OF PLASTICIZERS IN CELLULOSE ACETATE BUTYRATE (37 PER CENT BUTYRYL, 13 PER CENT ACETYL) FILMS IMMERSSED IN WATER AT 40° C.

A, Dibutyl sebacate
B, Diamyl phthalate
C, Butyl phthalyl butyl glycollate
D, Triphenyl phosphate
E, o-Cresyl-p-toluene sulfonate

TABLE III. COMPATIBILITY OF PLASTICIZERS WITH CELLULOSE ACETATE

	Max. Compatibility ^a						Max. Permanent Compatibility (High Acetyl)
	Used			Found			
	H	M	L	H	M	L	
<i>Part plasticizer/100 parts cellulose acetate</i>							
Benzophenone	60	60	60	60	50	50	20
Butyl phthalyl butyl glycolate	60	50	30	60	50	25	50
Camphor	30	30	30	30	30	30	5
<i>o</i> -Cresyl- <i>p</i> -toluene sulfonate	30	40	40	30	40	40	30
Cyclohexyl- <i>p</i> -toluene sulfonamide	30	30	30	30	30	30	30
Diamyl phthalate	20	10	10	20	10	10	20
Dibutyl phthalate	30	20	20	30	20	20	30
Dibutyl sebacate	<10	<10	<10	<10	<10	<10	<10
Dibutyl succinate	30	30	20	30	30	20	5
Dibutyl tartrate	90	90	90	90	90	90	25
Diethoxyethyl adipate	40	40	30	40	40	30	5
Diethoxyethyl phthalate	70	70	70	70	70	70	25
Diethyl adipate	90	80	60	65	65	40	0
Diethyleneglycol dipropionate	90	90	90	65	65	75	2
Diethyl phthalate	90	90	90	85	85	85	30
Diethyl sebacate	20	10	10	20	10	10	10
Diethyl succinate	100	100	100	20	20	20	0
Diethyl tartrate	100	100	100	90	95	100	5
Dimethoxyethyl adipate	90	90	90	90	90	90	5
Dimethoxyethyl phthalate	100	100	100	100	100	100	25
Dimethyl phthalate	100	100	100	85	90	90	15
Dipropyl phthalate	80	70	50	75	70	50	35
Ethyl benzoyl benzoate	50	50	50	50	50	50	50
Ethylene glycol diacetate	100	100	100	15	15	15	0
Ethylene glycol dibutyrate	80	70	60	30	30	35	5
Ethylene glycol dipropionate	100	100	100	15	15	15	0
Ethyl phthalyl ethyl glycolate	100	100	100	100	100	100	40
Methyl benzoyl benzoate	70	70	70	70	70	70	55
Methyl phthalyl ethyl glycolate	100	100	100	100	100	100	40
<i>o</i> - & <i>p</i> -Toluene ethyl sulfonamide	100	100	100	100	100	100	35
Triacetin	100	100	100	95	100	100	12
Tributyl citrate	50	40	30	50	40	30	30
Tributyl phosphate	80	80	80	70	70	70	17
Tributyryl	60	40	30	60	40	30	25
Tricresyl phosphate	30	20	20	25	20	20	20
Triethylene glycol diacetate	100	100	100	100	100	95	5
Triethylene glycol dibutyrate	70	70	70	70	70	70	7
Triethylene glycol dipropionate	90	90	90	90	90	90	7
Triphenyl phosphate	50	50	45	35	35	40	30
Tripropionin	90	90	90	80	80	85	25

^a H, high acetyl (40.5%); M, medium acetyl (38.5%); L, low acetyl (37.5%).

these figures with those for cellulose acetate will illustrate the increased strength of the plastic by virtue of the low quantity of plasticizer used, and the advantages of permanence and resistance to water offered by the more desirable plasticizers.

Experimental Procedure

Procedures for laboratory tests employed in this investigation are as follows:

REFRACTIVE INDICES of liquid plasticizers were determined at 25° C. on an Abbe refractometer. Values for those plasticizers which are solids under ordinary conditions were obtained at 25° C. on supercooled melts where possible and in other cases at their respective melting points.

FREE ACIDITY. Duplicate 10-gram samples of the plasticizers were dissolved in 100 cc. of ethyl alcohol, and the free acidity was titrated with 0.1 *N* sodium hydroxide using 10–15 drops of phenolphthalein indicator. Blanks were run on the reagents. The net amount of alkali was calculated to the "free acidity number", the number of cubic centimeters of normal alkali required to neutralize the acidity in a 100-gram sample.

Some of the esters saponify slowly under these conditions and result in fading end points. In such cases the accuracy is poor and the free acidity numbers tend to be high. It is best to titrate rapidly to the

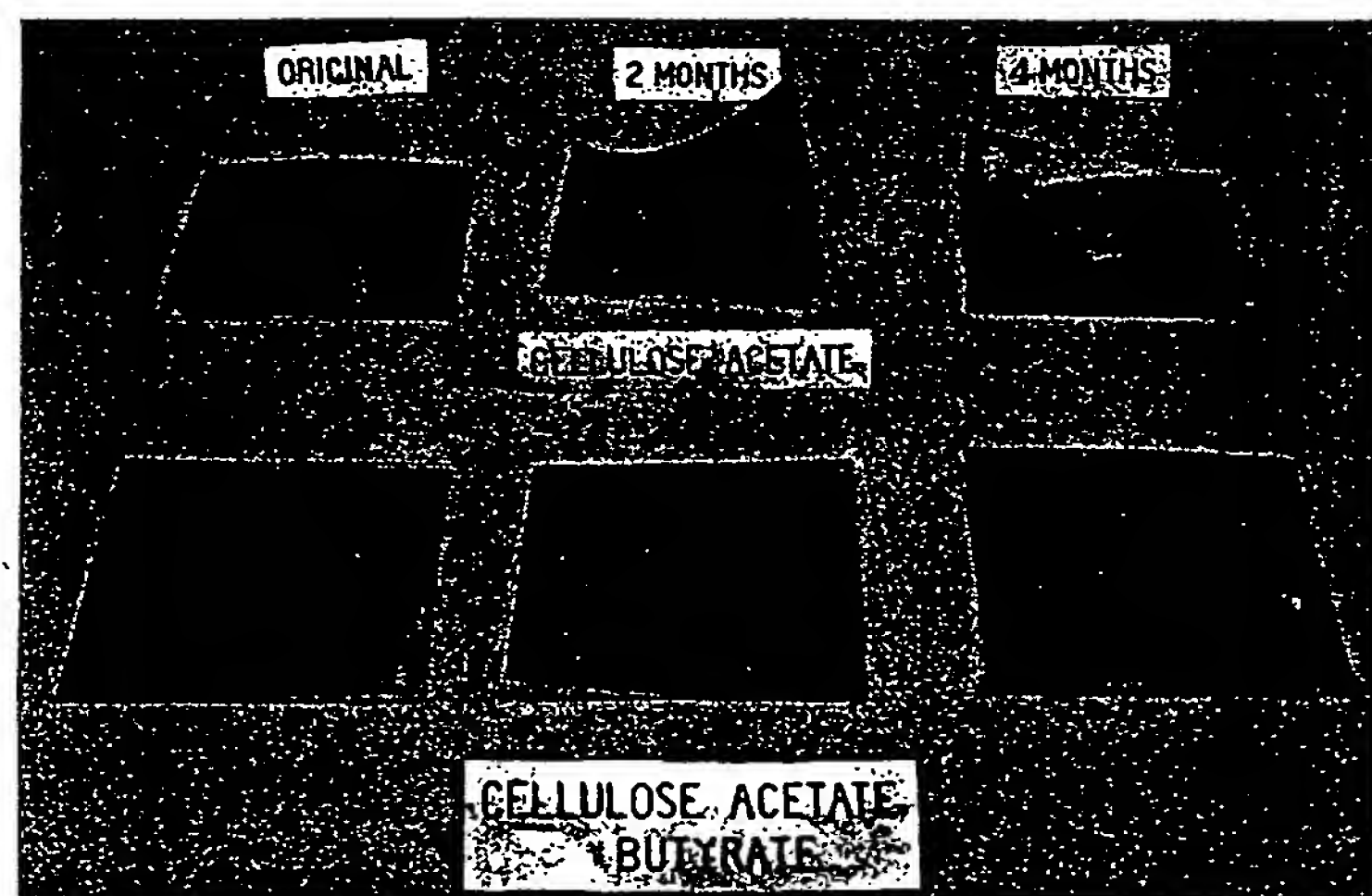
first good end point and take the value thus observed.

BOILING WATER STABILITY. Ten-gram samples of the plasticizers were refluxed for 24 hours with 100 cc. of distilled water, and the mixtures were titrated while warm with 0.1 *N* alkali, using phenolphthalein indicator. Blanks were run and the net amount of alkali used was calculated to cubic centimeters of normal alkali required to neutralize the acidity developed by a 100-gram sample. From this value was subtracted the free acidity value obtained by previous test, and the difference recorded as the boiling water stability.

COMPATIBILITY WITH CELLULOSE ACETATE. Samples of film were coated from acetone solutions of cellulose acetate of high (40.5 per cent), medium (38.5 per cent), and low (37.5 per cent) acetyl contents containing increasing quantities of each plasticizer. The films were examined after evaporation of the solvent to determine the maximum quantity of plasticizer which would give a clear film. Films of this maximum plasticizer content were then prepared, and after complete curing by incubation for 18 hours in an oven at 55° C., the plasticizer contents were determined by analysis. Agreement on duplicate tests was found to be reliable within 5 per cent, and results here obtained were therefore rounded off to the nearest even 5 per cent plasticizer content as the maximum compatibility.

PLASTICIZER RETENTION TESTS. Films of known plasticizer content, obtained as described above, were prepared for retention tests by cutting pieces approximately 3 inches (7.6 cm.) square for water immersion, oven incubation, and roof exposure samples. All retention samples were then identified by suitable marking and were weighed on an analytical balance.

Roof exposure samples were placed on an out-of-door exposure frame and washed at intervals to remove surface dirt, dried 2 hours at 55° C., and weighed. Losses in weight were calculated as plasticizer loss.



SHEETS OF CELLULOSE ACETATE (TENITE I) AND CELLULOSE ACETATE BUTYRATE (TENITE II) PLASTIC DURING EXPOSURE TESTS

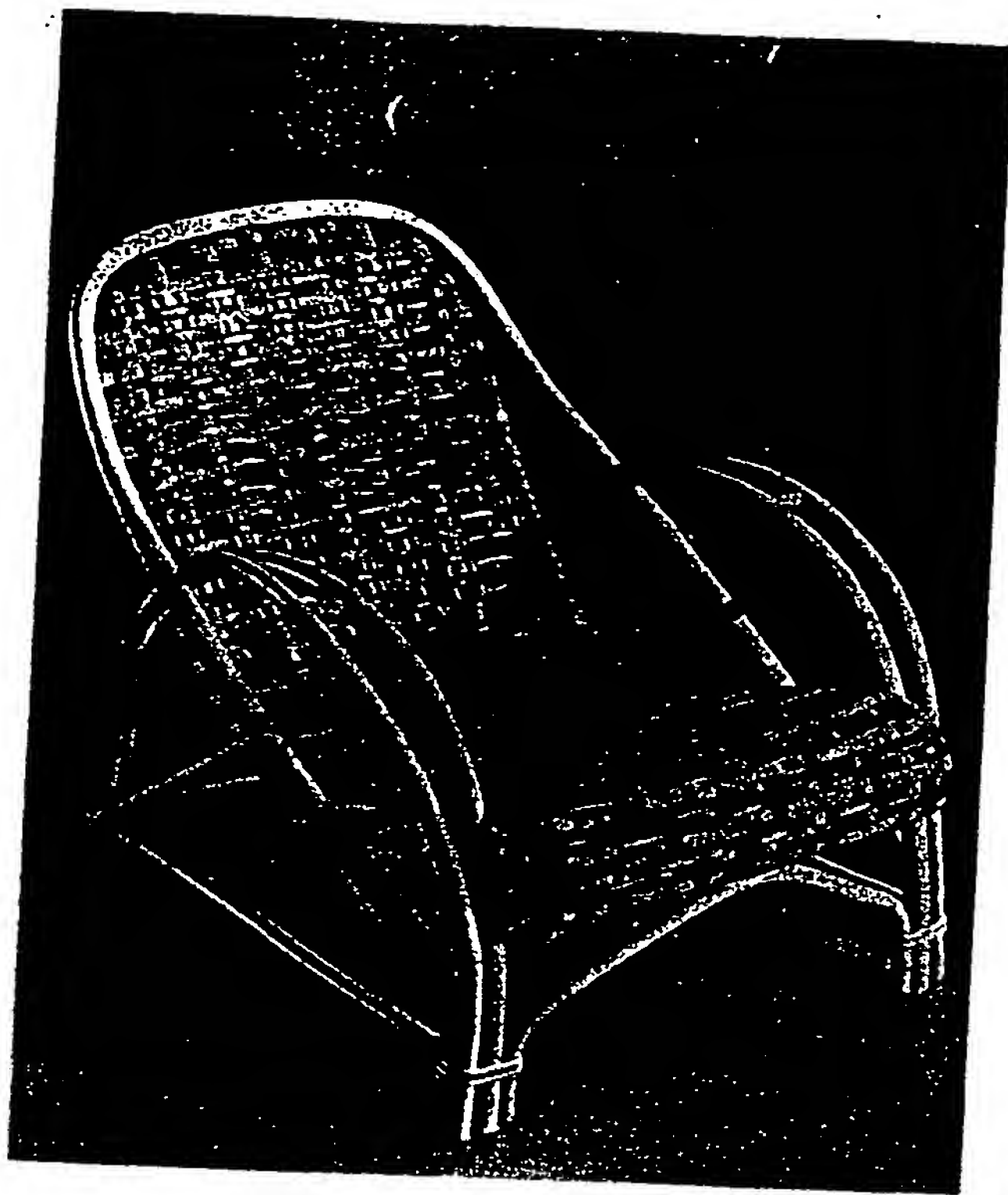
That the loss in weight of the films was a reliable measure of plasticizer loss was demonstrated by analysis of a series of test samples before and after water immersion, as follows:

WATER SOLUBILITY. In a 3-liter round-bottom flask 1000 cc. of distilled water were agitated vigorously with a mechani-

[illegible]

Parts plasticizer/ 100 parts base	Dimethyl Phthalate						Diethyl Phthalate						Dimethoxyethyl Phthalate					
	Cellulose acetate			Cellulose acetate butyrate			Cellulose acetate			Cellulose acetate butyrate			Cellulose acetate			Cellulose acetate butyrate		
Flow temp., ° F.	266	285	307	266	285	307	266	285	307	266	285	307	266	285	307	266	285	307
% elongation	8.0	6.5	5.0	23.8	22.7	21.8	40.0	28.6	20.8	26.2	24.7	23.4	49.2	33.3	25.0	28.9	26.7	24.6
Tensile strength, lb./sq. in.	6,630	8,100	9,930	4690	5520	6,540	2860	3850	5100	4410	5340	6,470	2760	3700	4880	3710	4680	5,870
Flexural strength, lb./sq. in.	11,140	14,200	17,000	7840	9240	10,950	3930	6050	8800	7390	8920	10,800	3670	5700	8390	6430	8240	10,480
Rockwell hardness M	79.5	90.5	101.1	72.4	80.1	86.4	49.0	59.7	75.5	65.5	75.2	84.3	20.6	44.3	67.2	60.1	71.2	82.0
% water absorption (48 hr.)	2.13	2.47	3.24	1.45	1.58	1.68	1.78	2.13	2.38	1.40	1.48	1.82	2.64	2.90	3.23	1.58	1.73	1.79
% leaching (48 hr.)	0.58	0.52	0.45	0.41	0.29	0.22	2.18	1.11	0.52	0.33	0.27	0.20	1.98	1.62	0.51	0.26	0.20	0.15
% loss in wt. (1 wk. at 150° F.)	2.40	0.86	0.53	1.06	0.60	0.46	6.67	3.85	1.96	0.54	0.40	0.21	0.41	0.34	0.23	0.19	0.17	0.13
% shrinkage (1 wk. at 150° F.)	1.38	0.11	0.09	0.89	0.48	0.19	3.02	1.53	0.70	0.33	0.27	0.13	0.29	0.21	0.17	0.13	0.11	0.09

	Dibutyl Phthalate			Diamyl Phthalate			Triphenyl Phosphate			Tricresyl Phosphate			Dibutoxyethyl Phthalate			Dibutyl Sebacate		
Parts plasticizer/100 parts base	21.0	14.6	8.1	21.5	15.0	8.3	22.5	15.3	8.8	27.4	19.2	11.6	22.6	15.7	9.3	23.6	16.5	9.5
Flow temp., ° F.	266	285	307	266	285	307	266	285	307	266	285	307	266	285	307	266	285	307
% elongation	36.0	30.0	25.8	37.6	30.5	26.6	34.0	27.0	20.0	48.8	33.0	26.7	32.5	29.0	25.8	66.5	46.0	34.2
Tensile strength, lb./sq. in.	4280	5250	6,380	4220	5180	6,340	4500	5450	6,300	3580	4550	5760	3270	4250	5,460	3340	4320	5540
Flexural strength, lb./sq. in.	6380	8160	10,420	6240	8080	10,330	7200	8850	10,700	5000	7100	9700	5320	7470	10,100	3500	5400	7820
Rockwell hardness M	57.6	69.4	80.7	56.5	69.2	80.4	72.0	80.7	87.5	48.9	62.4	76.5	54.6	66.2	78.8	40.7	57.0	74.4
% water absorption (48 hr.)	1.25	1.38	1.80	1.22	1.35	1.83	1.34	1.44	1.63	1.18	1.27	1.50	1.37	1.49	1.62	1.38	1.48	1.60
% leaching (48 hr.)	0.27	0.22	0.19	0.20	0.18	0.14	0.08	0.08	0.08	0.08	0.07	0.07	0.08	0.07	0.05	0.22	0.19	0.13
% loss in wt. (1 wk. at 150° F.)	0.52	0.45	0.36	0.51	0.43	0.34	0.14	0.13	0.11	0.13	0.12	0.10	0.16	0.13	0.09	0.38	0.25	0.15
% shrinkage (1 wk. at 150° F.)	0.41	0.29	0.10	0.39	0.28	0.14	0.08	0.06	0.05	0.05	0.02	0.0	0.08	0.07	0.05	0.07	0.05	0.03



LAWN CHAIR MADE OF CELLULOSE ACETATE BUTYRATE
(TENITE II) PLASTIC

cal stirrer, and the plasticizer to be tested was added in drops from a weighed quantity of sample. Each addition of plasticizer was thoroughly mixed and then allowed to stand until any insoluble droplets were completely separated at the top or bottom. To aid in identifying the first appearance of small drops of oil, a water-insoluble red dye was added either to the water or to the plasticizer before its addition to the water. From the quantity of sample required to produce a visible drop of insoluble plasticizer, its solubility was calculated.

In testing plasticizers which are solids at ordinary temperatures, the sample to be tested was heated on a steam bath to 80° C. before addition to the water.

TENSILE STRENGTH AND ELONGATION. Tests were run with a Tinius Olsen Universal hydraulic testing machine in accordance with A. S. T. M. method D-48-37 except for the following modifications: A dry sample taken immediately after processing and molding was placed in a desiccator for a minimum of 8 hours for conditioning. The test specimen was cut from the pressed slab to dimensions of 0.50 × 0.20 × 5.0 inches (1.27 × 0.51 × 12.7 cm.), and the central portion ground down to 3/8 inch (9.53 mm.) in width and clamped in jaws 3 inches (7.62 cm.) apart. The crosshead speed was 0.50 inch per minute. Elongation was measured and reported in per cent at point of breakage, as calculated from the distance through which the jaws had moved and the original distance between the jaws.

FLEXURAL STRENGTH. Tests were run on a Tinius Olsen Universal hydraulic testing machine in accordance with A. S. T. M. method D-48-37, with modifications of conditioning, size of test specimen, and crosshead speed as reported above. Supports were 1.5 inches (3.8 cm.) apart.

ROCKWELL HARDNESS. Tests were run with a Wilson Rockwell hardness tester model IR in accordance with

A. S. T. M. method D-229-37T, except that a specimen 3/16 inch (4.7 mm.) thick was used, and the machine was adjusted so that the major load was applied in 10 seconds. The major load was then released and the reading taken 10 seconds later.

All tests were run on the M scale which involves using a 1/4-inch (6.35-mm.) ball penetrator, a minor load of 10 kg., and a major load of 100 kg., and taking readings on the red scale.

WATER ABSORPTION AND LEACHING. Two dry specimens, 0.75 × 0.20 × 4.75 inches (1.91 × 0.51 × 12.1 cm.) were weighed and immersed in 1 liter of water at 25° ± 2° C. After 48 hours the specimens were taken out, dried with lintless cloth, and weighed. Per cent water absorption was calculated from the difference in weights. The above specimens were then dried in an oven at 65.6° C. (150° F.) for 48 hours, cooled to room temperature in a desiccator, and weighed again. Per cent leaching was calculated from the difference in weight from the original weight.

Although the figure for water absorption as obtained by this procedure is useful for comparison, it is apparent and not actual. The actual water absorbed is greater than indicated because no allowance is made on this test for the amount of plasticizer leached out.

LOSS IN WEIGHT AND SHRINKAGE. Two dry specimens, 0.75 × 0.20 × 4.75 inches, were weighed, measured lengthwise, and placed in an oven at 65.6° C. After one week the specimens were transferred to a desiccator, allowed to cool to room temperature, and then weighed and measured again.

Per cent loss in weight was calculated from the difference in weights and the original weight. Per cent shrinkage was calculated from the difference in lengths and the original length.

FLOW TEMPERATURE OF THERMOPLASTIC MOLDING MATERIALS. This test determines the temperature at which a thermoplastic material attains a standard consistency as indicated by rate of extrusion into an orifice. By standard consistency is meant a definite degree of flowability such that when the material is subjected to a defined pressure in a defined extrusion mold the amount of flow in a defined time is constant.

Measurements of consistency were made at three temperatures, and the temperature of standard consistency was obtained by graphic interpolation. The apparatus used was the Rossi-Peakes flow tester¹. The test specimens were molded in the form of cylinders, 3/8 inch in diameter and 3/8 inch high.

All test specimens were conditioned at room temperature in a dry atmosphere over anhydrous calcium chloride for 72 hours. A working pressure of 1500 pounds per square inch (105.5 kg. per sq. cm.) was used. The unit of flow time was taken as 2 minutes. The test specimens at room temperature were inserted in the hot charge chamber and run immediately. Between runs the orifice was swabbed with acetone to remove any residual plasticizer or lubricant. Each material was run at three temperatures at which the flow fell within the interval 0.50 to 1.50 inches (1.27 to 3.81 cm.). The flow in inches was plotted against temperature in ° F. The temperature where flow was exactly 1.0 inch (2.54 cm.) was reported as the flow temperature.

PRESENTED as part of the Symposium on Cellulose Plastics before a joint session of the Divisions of Paint and Varnish Chemistry and of Cellulose Chemistry at the 99th Meeting of the American Chemical Society, Cincinnati, Ohio.

¹ U. S. Patent 2,066,016 (Dec. 29, 1936).